



AFRL-OSR-VA-TR-2014-0230

Advanced Metacrytal Media for Aerospace applications

David Smith
DUKE UNIVERSITY

09/17/2014
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTD
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE				<i>Form Approved</i> OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 09/15/2014		2. REPORT TYPE Final		3. DATES COVERED (From - To) 07/15/09 - 03/31/14	
4. TITLE AND SUBTITLE Advanced MetaCrystal Media for Aerospace Applications				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-09-1-0562-01	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Smith, David R.				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Duke University 2200 West Main Street, Suite 210 Durham, North Carolina 27705-4677				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Arlington, Virginia 22203				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT We propose a broad and comprehensive program to investigate a variety of topics relating to advanced metamaterials. We have selected topics across the electromagnetic spectrum—with a particular emphasis in the microwave regime—in which we will apply a variety of design, fabrication and characterization methods to develop new metamaterial paradigms. In one research thrust, we propose the development of hybrid, anisotropic MetaCrystals for optical and quasi-optical devices. MetaCrystals are the metamaterial analog of natural crystals that serve as critical components in optical technologie					
15. SUBJECT TERMS Keywords: Nonlinear metamaterials; metamaterial imager; computational imager; non-local electron response; hydrodynamic mc					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON David R. Smith
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code) 919-660-8258

Advanced MetaCrystal Media for Aerospace Applications

FA9550-09-1-0562

PI: David R. Smith

FINAL REPORT

Final Report

The purpose of the MetaCrystal Media program was to develop and investigate hybrid metamaterials—metamaterials that could provide advanced functionality by incorporating core materials with properties of interest—such as nonlinearity or tunability—into artificially structured metamaterials. Metamaterials provide a means of creating unique electromagnetic response, which can be used to manipulate and control electromagnetic waves propagation. In addition, metamaterials can concentrate electromagnetic or optical fields into highly localized regions where they can interact strongly with materials. This interaction can be harnessed to create multifunctional metamaterials.

Nonlinear Metamaterials

One of the first studies performed within this program was the use of nonlinear materials to form artificial nonlinear optical materials. We developed a comprehensive analytic theory and design methodology for nonlinear metamaterials, as well as a suite of computational techniques that allowed for the precise design and characterization of nonlinear metamaterial composites. We applied these tools in the design and demonstration of numerous nonlinear metamaterial structures, including the first experimental demonstration of phase matching with a negative index nonlinear metamaterial and the demonstration of harmonic generation in a material with index near zero. The initial metamaterial samples were made to operate at microwave frequencies, and utilized varactor diodes as the nonlinear component. By placing varactor diodes across the capacitive gaps in metamaterial samples, an artificial nonlinear metacrystal can be formed and its properties compared with theoretical predictions. To support this effort, a retrieval method was devised, allowing the assignment of the effective nonlinear susceptibility to a metamaterial sample based on the harmonics produced when excited by a fundamental wave. Using this retrieval, near exact agreement was demonstrated between theory and experimentally measured samples. The results of this study proved the ability to design and characterize artificial nonlinear crystals.

Nonlinear Optical Plasmonic Metamaterials

After demonstrating the basic concepts behind nonlinear metamaterial design, we began a program to develop an understanding of nonlinear metamaterials at infrared (IR) and visible wavelengths. At these wavelengths, metal response becomes significantly more complicated, and more detailed models of electron response must be incorporated into full-wave simulations. Moreover, metals possess some of the largest third-order nonlinear susceptibilities in materials, and can also yield very large second-order nonlinear susceptibilities when structured on the nanoscale (due to surface effects). As part of our program, we developed a set of numerical tools to investigate the nonlinear response of optical metamaterials, treating the metal using a semiclassical model of electron response. In particular, a hydrodynamic model was applied, in which the electron gas is treated as non-compressible and an electron pressure term is added to



the equation of motion. Within this model, nonlinear terms within the hydrodynamic equations can be retained and used to predict various nonlinear effects. We applied the model to understand the origin of second harmonic generation in metamaterial structures at optical wavelengths, confirming the empirically obtained experimental results of the Karlsruhe group (M. Wegener). A variety of nonlinear metallic configurations were considered as part of this effort, which continues now in the follow-on AFOSR program.

Nonlocal Response and the Extreme Coupling Limit

In the quest to understand the inherent nonlinear response of metals at optical wavelengths, we found it was necessary to make use of the hydrodynamic model of electron response. This model introduces an electron pressure term into the equations that results in the effective dielectric function being non-local—that is, having a dependence on wave-vector in addition to frequency. The nonlocal response of the dielectric function requires the imposition of additional boundary conditions at the interface between the nonlocal dielectric and other materials, resulting in a more complicated computational problem. As part of this program, we developed a simulation approach for nonlocal media, and made use of the approach to compute the properties of nonlinear composites as described in the previous section. However, the nonlocal electron response also has implications for linear optical scattering, though those effects are typically insignificant.

To probe the nonlocal response directly, we made use of the film-coupled nanoparticle system, using self-assembled monolayers to create uniform spacers between a collection of nanoparticles and a gold film. The layer-by-layer assembly technique allowed control over the spacing in increments of roughly a few Ångströms. Even greater control could be achieved using carbon chains terminated with amine groups on one side and thiol groups on the other, such that spacer layers could be produced with control to the Ångström level. Studying the plasmon resonance shift associated with this film-coupled nanoparticle system as a function of spacer layer, we were able to probe the extreme coupling limit, where the nanoparticles were spaced at distances between 0.5 and ~25 nm, with Ångström level precision. Approach curves indicated a failure of the classical model of electron response, and consistency with the nonlocal response (contained in the hydrodynamic model). While there is much to be done to further understand this important phenomena, the experiment (published in *Science*) brought to the forefront the need for new models for the metal response in nanostructured plasmonic systems having extreme feature sizes (e.g., sub-nanometer gaps).

Film-Coupled NanoCube System

The film-coupled nanoparticle system provides an unprecedented, unparalleled means of controlling the enhancement region in plasmonics and optical metamaterials. The entire range of plasmonic effects, including surface enhanced Raman scattering (SERS), fluorescence enhancement, nonlinear enhancement and many others—all such effects are tied to the details of the field enhancement that occurs in the sub-nanometer gaps between plasmonic nanoparticles. Because the film-coupled nanoparticle system relies on planar fabrication for the gap (or spacer) layers, a variety of surface chemistries can be used to create films with precisely controlled thickness; alternatively, deposition techniques, such as atomic layer deposition (ALD) can be leveraged to achieve Ångström level control over the layer thicknesses. In this program, we have investigated both techniques and shown that control can be exerted over the enhancement region to the sub-nanometer scale.



Film-coupled nanospheres were used to demonstrate the impact of non-local response; however, the film-coupled nanosphere system does not provide many degrees of freedom to enhance other phenomena. For example, the field enhancement is tied directly to the plasmon resonance shift in the film-coupled nanosphere system: If the sphere diameter is changed, or the gap, both the resonance and the field enhancement are changed, making it difficult to perform optimization where both the resonance and field enhancement need to be tuned separately.

The film-coupled nanocube system possesses entirely distinct properties from that of the film-coupled nanosphere. The nanocube, being a planar particle, supports transmission-line modes between the nanocube and film, whose resonance frequencies depend entirely on the nanocube width. The field enhancement is separately controlled via the gap thickness, allowing for enhancement effects to be tuned and optimized. As part of this program, we have developed a comprehensive theoretical framework for the optical patch antenna (of which the film-coupled nanocube is an example), as well as extending the simulation tools to accommodate this geometry. We have also performed an experiment showing the potential use of the nanocubes as a “perfect absorber” medium, with the advantage that such a medium can be achieved through self-assembly rather than lithography (this work was published in *Nature*). The film-coupled nanocube system can be used as the basis for ultra-bright light emitting diodes (LEDs) or efficient detectors. We have also performed a number of experimental studies to explore and confirm the unique modes associated with film-coupled nanocubes. This work continues on into the follow-on AFOSR program.

Metamaterial Computational Imaging System

As part of this program, we have investigated the use of metamaterials as the basis of a new type of aperture for computational imaging schemes. The metamaterial aperture consists of either a one dimensional waveguide (such as a microstrip) or a two dimensional waveguide (such as a parallel plate waveguide), with complementary metamaterial elements patterned into the upper conductor. Because these metamaterial elements resemble irises, they allow radiation to leak from the waveguide mode into the free space region to be imaged. The configuration is reminiscent of a leaky-wave antenna, however the sub-wavelength metamaterial elements are densely packed, and their resonances dominate the dispersive properties of the aperture. The metamaterial elements are patterned such that the resonance frequency of each of the elements is assigned randomly over the operating bandwidth (in this case, 18-26 GHz). As a function of frequency, then, the radiated mode pattern has low gain with a random set of nodes that move around in space as the frequency is varied. Because there is sufficient diversity in the modes, they can be used to encode distinct scene information; that is, an image can be formed simply by conducting a frequency sweep over a suitably large bandwidth, with the image reconstructed using standard computational image estimation.

The metamaterial imager concept has grown out of the legacy of AFOSR funding, starting with the complementary metamaterial waveguide structures initiated in a previous AFOSR program and expanded in the present program. The metamaterial aperture has potential advantages over conventional technology, in that it utilizes a small number of transceivers (possibly just one), and has no moving or scanning mechanical components. To confirm the imaging concept, we performed an imaging experiment using a one-dimensional aperture that could provide a low-resolution image in the range and one angular variable (1+1 dimensions). It was shown that a retroreflector could be tracked, at 10 frames-per-second, using just the frequency sweep (frequency diversity) and compressive imaging techniques. That is, the scene was vastly



undersampled for the experiment. This work was published in Science, and represents the first report of the frequency-diverse metamaterial imager.

Subsequently, a two-dimensional metamaterial imager system was built, and was used to demonstrate the ability to resolve full three-dimensional images (range+two angular variables). This system consisted of two metamaterial panels and a single low gain probe. Simple metal objects were imaged, showing that the metamaterial imager should be capable of ultimately state-of-the-art resolution.

During the time when this research was being conducted, representatives from the Department of Homeland Security and the Transportation Safety Division visited our lab and became interested in the imaging concept. This led to a very large program, jointly funded by DHS and TSA, to develop next-generation mm-wave imagers for aviation security. As an outgrowth of the AFOSR research, we are now deeply involved in the full system design of a functioning scanner, appropriate for current airport security requirements. As part of this program, we are building a full-scale demonstration unit (1.6 m x 1.6 m), with complete software support, standalone radio, and integrated automated threat detection (ATD) software. This work has also led to a spinoff company, Evolv Technology (Boston, MA), working to develop commercial units based on the underlying technology.

Publications on Grant

Circular dichroism in the third-order nonlinear properties of a metamaterial

A. Rose, D. R. Smith, D. A. Powell, I. V. Shadrivov, Y. S. Kivshar

Physical Review B **88**, 195148 (2013)

Forward and backward unidirectional scattering from plasmonic coupled wires

E. Poutrina, A. Rose, D. Brown, A. Urbas, D.R. Smith

Optics Express **21**, 31138 (2013)

Analysis of scattering from optical plasmonic patch antennas

C. Ciraci, B. Lassiter, A. Moreau, D. R. Smith

Journal of Applied Physics **114**, 163108 (2013)

Plasmonic Waveguide Modes of Film-Coupled Metal NanoCubes

J. B. Lassiter, F. McGuire, J. J. Mock, C. Ciraci, R. T. Hill, B. J. Wiley, A. Chilkoti, D. R. Smith

Nano Letters **13**, 5866 (2013)

Effects of classical nonlocality on the optical response of three-dimensional plasmonic nanodimers

C. Ciraci, Y. Urzhumov, D. R. Smith

Journal of the Optical Society of America B **30**, 2731 (2013)



Surfaces, films, and multi-layers for compact nonlinear plasmonics

X. Liu, E. Poutrina, A. Rose, C. Ciraci, S. Larouche, D. R. Smith

Journal of the Optical Society of America B **30**, 2999 (2013)

Subwavelength plasmonics for graded-index optics on a chip

M. Grajower, G. M. Lerman, I. Goykhman, B. Desiatov, A. Yanai, D. R. Smith, U. Levy

Optics Letters **38**, 3492 (2013)

Metamaterial Apertures for Compressive Imaging

G. Lipworth, J. D. Hunt, T. Driscoll, A. Mrozack, D. Brady, D. R. Smith

Journal of the Optical Society of America A **30**, 1603 (2013)

Homogenization analysis of complementary wave guide metamaterials

N. Landy, J. Hunt, D. R. Smith

Photonics and Nanostructures, Fundamentals and Applications **11**, 453 (2013)

Hydrodynamic model: A macroscopic approach to a microscopic problem

C. Ciraci, J. B. Pendry, D. R. Smith

ChemPhysChem **14**, 1109 (2013)

Nonlinear interference and unidirectional wave-mixing in metamaterials

A. Rose, D. Huang, D. R. Smith

Physical Review Letters **110**, 063901 (2013)

Nonlocality in metallo-dielectric multilayered structures

A. Moreau, C. Ciraci, D. R. Smith

Physical Review B **87**, 045401 (2013)

Compressive metamaterial imager

J. Hunt, A. Mrozack, G. Lipworth, T. Driscoll, M. Reynolds, D. Brady, D. R. Smith

Science **339**, 310 (2013)

Second-harmonic generation in metallic nanoparticles: Clarification of the role of the surface

C. Ciraci, E. Poutrina, M. Scalora, D. R. Smith

Physical Review B **86**, 115451 (2012)

Plasmon ruler with Angstrom length resolution

R. T. Hill, J. J. Mock, A. Hucknall, S. D. Wolter, N. M. Jokerst, D. R. Smith, A. Chilkoti

ACS Nano **6**, 9237 (2012)

Current oscillations in vanadium dioxide: Evidence for electrically triggered percolation avalanches

T. Driscoll, J. Quinn, G. Seo, Y.-W. Lee, H.-T. Kim, D. R. Smith, M. Di Ventra, D. N. Basov

Physical Review B **86**, 094203 (2012)

Nonlinear magnetoelectric metamaterials: Analysis and homogenization via a microscopic coupled-mode theory

A. Rose, S. Larouche, E. Poutrina, D. R. Smith

Physical Review A **86**, 033816 (2012)

Probing the ultimate limits of plasmonic enhancement



C. Ciracì, R. Hill, J. J. Mock, A. Dominguez, Y. Urzhumov, S. Maier, J. B. Pendry, A. Chilkoti, D. R. Smith

Science **337**, 1072 (2012)

Cover Article

Demonstration of nonlinear magneto-electric coupling in metamaterials

A. Rose, D. Huang, D. R. Smith

Applied Physics Letters **101**, 051103 (2012)

Cover Article

Controlled reflectance surfaces with film-coupled colloidal nanocubes

A. Moreau, J. J. Mock, R. Hill, C. Ciracì, B. Wiley, A. Chilkoti, D. R. Smith

Nature **492**, 86 (2012)

Origin of Second harmonic generation enhancement in optical split-ring resonators

C. Ciracì, E. Poutrina, M. Scalora D. R. Smith

Physical Review B **85**, 201403(R) (2012)

Enhancement of four-wave mixing processes by nanoparticle arrays coupled to a gold film

E. Poutrina, C. Ciraci, D. Gauthier, D. R. Smith

Optics Express **20**, 11005 (2012)

Probing dynamically tunable localized surface plasmon resonances of film-coupled nanoparticles by evanescent wave excitation

J. J. Mock, R. T. Hill, Y.-J. Tsai, A. Chilkoti, D. R. Smith

Nano Letters **12**, 1757 (2012)

Design and experimental characterization of nonlinear metamaterials

D. Huang, E. Poutrina, H. Zheng, D. R. Smith

Journal of the Optical Society of America B **28**, 2925 (2011)

Quantitative study of the enhancement of bulk nonlinearities in metamaterials

A. Rose, S. Larouche, D. R. Smith

Physical Review A **84**, 053805 (2011)

Overcoming phase mismatch in nonlinear metamaterials

A. Rose, D. R. Smith

Optics Materials Express **1**, 1232 (2011)

Reconfigurable Gradient Index using VO₂ Memory Metamaterials

M. D. Goldflam, T. Driscoll, B. Chapler, O. Khatib, N. M. Jokerst, S. Palit, D. R. Smith, B.-J. Kim, G.

Seo, H.-T. Kim, M. Di Ventra, D. N. Basov

Applied Physics Letters **99**, 044103 (2011)

Controlling the second-harmonic in a phase-matched negative-index metamaterial

A. Rose, D. Huang, D. R. Smith

Physical Review Letters **107**, 063902 (2011)

Selected for Physics Viewpoint

Broadly tunable quasi-phase-matching in nonlinear metamaterials

A. Rose, D. R. Smith



Physical Review A **84**, 013823 (2011)

Wave mixing in nonlinear magnetic metacrystal

D. Huang, A. Rose, E. Poutrina, S. Larouche, D. R. Smith

Applied Physics Letters **98**, 204102 (2011)

Nonlinear oscillator model for metamaterials with a magnetic response: Experimental verification

E. Poutrina, D. Huang, Y. Urzhumov, D. R. Smith

Optics Express **19**, 8312 (2011)

Leveraging nanoscale plasmonic modes to achieve reproducible enhancement of light

R. Hill, J. J. Mock, Y. Urzhumov, D. S. Sebban, S. J. Oldenburg, S.-Y. Chen, A. A. Lazarides, A. Chilkoti, D. R. Smith

Nano Letters **10**, 4150 (2010)

Nonlinear parameter retrieval from three- and four-wave mixing in metamaterials

A. Rose, S. Larouche, D. Huang, E. Poutrina, D. R. Smith

Phys. Rev. E **82**, 036608 (2010)

Analysis of nonlinear electromagnetic metamaterials

E. Poutrina, D. Huang, D. R. Smith

New Journal of Physics **12**, 093010 (2010)

Experimental determination of the second order susceptibility for a varactor-loaded metamaterial

S. Larouche, A. Rose, E. Poutrina, D. Huang, D. R. Smith

Applied Physics Letters **97**, 011109 (2010)

Analysis of the power dependent tuning of a varactor-loaded metamaterial at microwave frequencies

D. Huang, E. Poutrina, D. R. Smith

Applied Physics Letters **96**, 104104 (2010)

